THE NDE OF COMPLEX LIQUIDS CONTAINING SUSPENDED PARTICLES

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INTRODUCTION

Many products of commercial significance exist as suspensions of particles in a liquid or will have consisted as such as suspension at a stage during manufacture; the particles may be solid or liquid. It is necessary to determine the physical state of such suspensions both in the development laboratory and for the purposes of quality and process control at plant level. Reliable estimates are required of the size distribution and concentration of the dispersed phase, as well as indications of flocculation, and network formation. Dynamic measures may be required in support of reaction processes such as crystallization. Techniques that can be used for the characterisation of suspensions are optical scattering or turbidity tests, sedimentation rate tests, ionizing radiation, electrical tests, electroacoustic measurements, and acoustic (ultrasonic) methods alone. Ultrasonic methods have the advantages that they can be used on mixtures that are too opaque for optical techniques, and that they can be incorporated into robust and low cost instrumentation. This paper gives a brief overview of the physics of the interactions of ultrasonic waves with particulate suspensions and a brief review of measurement methods and errors. Recent results that show agreement or otherwise between theory and experiment are given for silica sols. Examples are also given of the use of ultrasound to track flocculation in an aqueous emulsion, and to track a crystallization reaction.

THEORY

Ultrasonic studies of liquids generally require the measurement of the compression wave phase velocity $c(\omega)$ and/or the compression wave absorption or attenuation coefficient $\alpha(\omega)$, both as functions of frequency. The complex wave number for the liquid is

$$\beta = \frac{\omega}{c(\omega)} + i\alpha(\omega) \qquad (1)$$

where ω is the radian frequency ($\omega = 2\pi f$) and $i = \sqrt{-1}$. The change in phase velocity with

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respect to frequency is generally small and of the order of $1ms^{-1}$ over typical measurement bandwidths of tens of MHz. Whilst this compares to base velocity values of the order of $1000ms^{-1}$, the small changes that can be observed nevertheless can give useful indications of the physical state of a suspension. $\alpha(\omega)$ is generally more sensitive to state that $c(\omega)$. Both $\alpha(\omega)$ and $c(\omega)$ are affected by two sets of phenomena - those which result in the removal of energy from the wave in the form of heat, and those which result in scattering or reradiation of the wave in directions away from the ultrasound beam, and which appear to a receiver as attenuation because they do not impinge on its aperture. Ultrasound propagation in particulate mixtures is determined by some or all of a group of eight physical phenomena:

(a) Modification of the wavenumber due to the passage of the wave through the particles.
(b) Chemical relaxation in the continuous phase.
(c) Viscosity in the continuous phase.
(d) Contrast between compressibilities between the phases resulting in monopole reradiation.
(e) Pressure-temperature coupling leading to heat flux between phases.
(f) Pressure-temperature coupling leading to differential expansion of the phases and monopole reradiation.
(g) Density contrast between the phases leading to hydrodynamic losses and dipole reradiation.
(h) Particle resonances, leading to quadripole or higher order reradiation.

Where the suspended particles are of significantly higher density than the continuous phase (c) and (g) above, are the principal effects, and purely hydrodynamic theories [1-3] provide good predictions of wave number versus frequency. More recently effects (d) and (e) have been incorporated into a hydrodynamic approach [4] although comprehensive comparison between theory and experiment remains to be done. More comprehensive theories based on scattering ideas incorporate all of the effects noted above. The theory of Epstein and Carhart [5] applies to liquid particles and has been developed by Allegra and Hawley [6] so as to apply to either liquid or solid particles in a liquid continuum. The scattering theories have the disadvantage that they require detailed knowledge of the physical properties of both phases, and these are not always known with precision; the theories have the advantage that they apply to mixtures in which the difference between the densities of the two phases is low - a situation in which the hydrodynamic models mentioned above [1-3] do not apply. For mixtures to which both the scattering models and the hydrodynamic models apply we have found reasonable agreement between the models and with experiment. In this work we limit further consideration to the Allegra and Hawley formulation and calculate the wave number of the mixture using

$$\left(\frac{\beta}{k_c}\right)^2 = 1 + \frac{3\phi}{ik_cR^3}\left(A_0 + 3A_1 + 5A_2\right) - \frac{27\phi^2}{k_c^6R^6}\left(A_0A_1 + 5A_1A_2\right) - \frac{54\phi^2}{k_c^6R^6}\left(A_1^2 + \frac{5}{3}A_0A_2 + 3A_1A_2 + \frac{115}{21}A_2^2\right) \quad (2)$$

where k_c is the wave number of the continuous phase, ϕ is the volume concentration of

particles, R is the particle radius and A_n are the partial wave scattering coefficients [6]. The three lines of Equation 2 correspond to three classical formulations for the wave number [7-9]. For mixtures containing a range of particle sizes β is obtained by summing over all R, taking account of the dependence of A_n on R.

MEASUREMENT TECHNIQUES

The characterisation of particulate mixtures requires $\alpha(\omega)$ and/or $c(\omega)$ to be measured as functions of frequency in the range 1MHz to 100 MHz. This can be achieved through a series of spot frequency measurements or by means of wide bandwidth pulses analysed by Fourier techniques. Pulse-echo or through transmission systems can be used, and for this work we have used a short pulse spectrometer instrument described some years ago [10]. The errors associated with ultrasound measurements are complex and we will briefly consider those associated with the absorption coefficient $\alpha(\omega)$. Errors associated with $c(\omega)$ will be the subject of a future publication. $\alpha(\omega)$ is calculated from a measured spectrum $X(\omega)$ and a reference spectrum $X_0(\omega)$, thus

$$\alpha(\omega) = \frac{1}{d} \ln \frac{|X_0(\omega)|}{|X(\omega)|} \tag{3}$$

where d is the propagation distance between the ultrasonic transmitting and receiving transducers. Taking differentials we obtain

$$\frac{\Delta\alpha(\omega)}{\alpha(\omega)} = -\frac{\Delta d}{d} - \frac{\Delta|X_0(\omega)|}{|X_0(\omega)|} \cdot \frac{e^{\alpha(\omega)d}}{\alpha(\omega)d} \tag{4}$$

We interpret $|X_0(\omega)| / \Delta|X(\omega)|$ as the system signal-to-noise ratio (SNR). Thus the relative error in $\alpha(\omega)$ depends on the precision with which d is known, and the noise-to-signal ratio (NSR) multiplied by a magnifying factor $M = e^{\alpha(\omega)d} / \alpha(\omega)d$. The factor M is plotted versus the total measured attenuation αd in Figure 1. We note that for small and large αd the system noise will magnify greatly into large errors in $\alpha(\omega)$; this error generation becomes particularly acute for $\alpha(\omega)d > 3$ Nepers. Our spectrometer instrument is optimised to measure $\alpha(\omega)$ of the order of 30 Neper m^{-1}, with d fixed at 30mm.

EXPERIMENTS

In earlier publications we have reported excellent agreement between the Allegra and Hawley model, and other theoretical formulations in some cases, with experimental measurements in suspensions of polystyrene spheres [11], silica spheres [11], iron spheres [12], TiO_2 [12] and kaolin [13]. In this paper we present new data on aqueous suspensions of silica spheres, an ultrasonic study of flocculation and network formation in an aqueous emulsion of l-bromohexadecane, and the results of an experiment to crystallize $CuSO_4$ from aqueous solution.

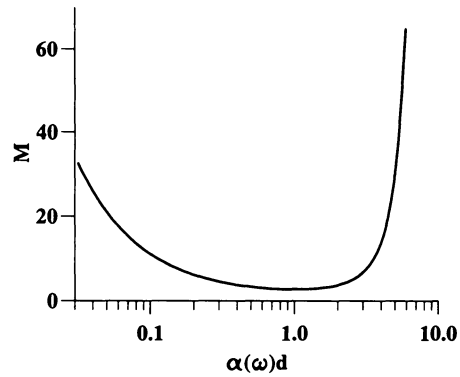

Figure 1. The error magnifying function $M=e^{\alpha(\omega)d}/\alpha(\omega)d$ versus $\alpha(\omega)d$.

Aqueous Suspensions of Silica Spheres

In earlier work [11] we have shown that the Allegra and Hawley model gives accurate simulations of ultrasonic wave propagation in aqueous suspensions of silica spheres at concentrations of 8% w/w, particle diameters in the range of 125nm to 320nm, and frequencies up to 20 MHz. We have extended this work to include studies of silica sols containing much smaller particles in the range 12nm to 30 nm diameter and we report some of our recent results here. Figure 2a shows experimentally measured absorption for a small particle sol, together with two simulations using the Allegra and Hawley model. The first is based on data used in our earlier study and is seen to over estimate $\alpha(\omega)$ by around 45%. The second simulation was based on the use of an effective continuous phase viscosity in the Allegra and Hawley model and is seen to be very nearly coincident with the experimental data. The viscosity function used in the fit was

$$\eta = \eta_0\left(1-\frac{\Phi}{p}\right)^{-2.5p}.A\left(1-e^{-bf}\right) \qquad (5)$$

η_0 is the viscosity of water and p is the particle volume packing fraction, around 0.6. A and b are constants which are adapted as the Allegra and Hawley model is fitted to experimental data. The first term in Equation 5 expresses the conventional dependence of viscosity on dispersed phase concentration [13]. The second term implies a viscosity that is a rising function of frequency in the tens of MHz range.

The viscosity function shown on Figure 2b corresponds to the lower fitted curve on Figure 2a. A viscosity that is a rising function of frequency is counter-intuitive and we are not at present in a position to explain it on the basis of new theory. We do, however, regard our experimental techniques as reliable and in the light of the excellent fits we have obtained between this adapted theory and experiment, further research will be undertaken to elucidate the underlying physical phenomena.

1 - bromohexadecane Emulsion

A 5% v/v aqueous emulsion of 1-bromohexadecane was flocculated by the addition of hydroxyethylcellulose (HEC) at either 0.026% v/v or 0.1% v/v. The reaction was

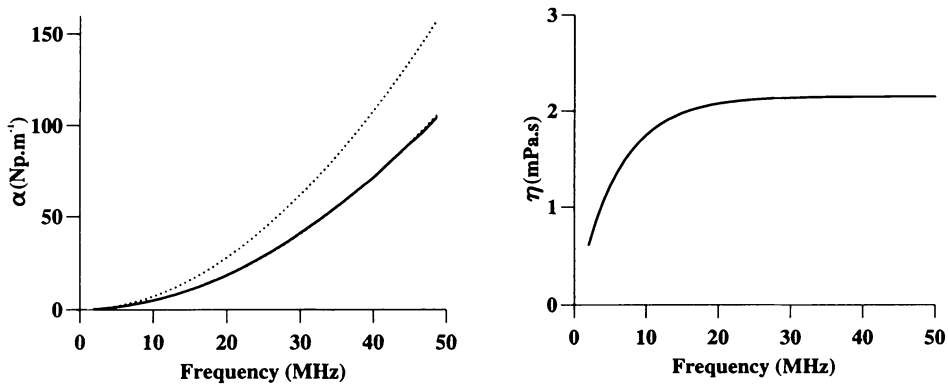

Figure 2. Left (a): absorption coefficient versus frequency for a silica sol 10% w/w spheres of 30nm diameter. The top dotted line shows the unadapted Allegra & Hawley simulation, whilst the lower dotted line shows the simulation adapted on viscosity which is coincident with the experimental data shown by the solid line. Right(b): fitted viscosity versus frequency.

followed by phase contrast microscopy to give a qualitative indication of the physical changes taking place during flocculation. For the lower dose of HEC the emulsion was seen to consist of a large population of base particles with diameters around 1.5μm and an evolving population of flocs formed of groups of base particles ("bunch of grapes") with an overall dimension which grew to around 15μm. The higher dose of HEC brought about a similar flocculation for the first ten minutes of the reaction after which the structure changed to form extended interconnected networks of suspended particles rather than discrete flocs. Ultrasonic absorption and phase velocity measurements were made at 1 minute intervals during these reactions, over bandwidths up to 50 MHz. The Allegra and Hawley theory, implemented as a computational model, was run adaptively using the Marquardt algorithm [14] with dispersed phase particle size as parameter so as to track the evolving particle size during the flocculation. The fit of the model could be achieved using either experimental attenuation or phase velocity data, and we present the latter here.

Figure 3a shows the change in velocity from its value at 2 MHz plotted versus frequency for 30 minutes of the lower dose flocculation. Figure 3b shows the fit of the Allegra and Hawley model to experimental data at 20 minutes of reaction with a two bin particle size distribution, compared to the simple monodisperse case. The particle sizes in the fit correspond to 1.5μm and 10μm. Figure 3c shows the fitted particle size as a function of time during the flocculation; the sizes observed by microscopy were seen to be of the same order as those obtained ultrasonically, although no formal image analysis has been performed at this stage. The higher dose emulsion behaved similarly for the first ten minutes of reaction, after which the fit between experimental and modelled data worsened, as extended networks rather than discrete particles formed in the flocculating mixture. The error associated with the fitting procedure is shown plotted versus time on Figure 3d. It is clear that the error could be used as a parameter to *indicate* network formation in a flocculating mixture.

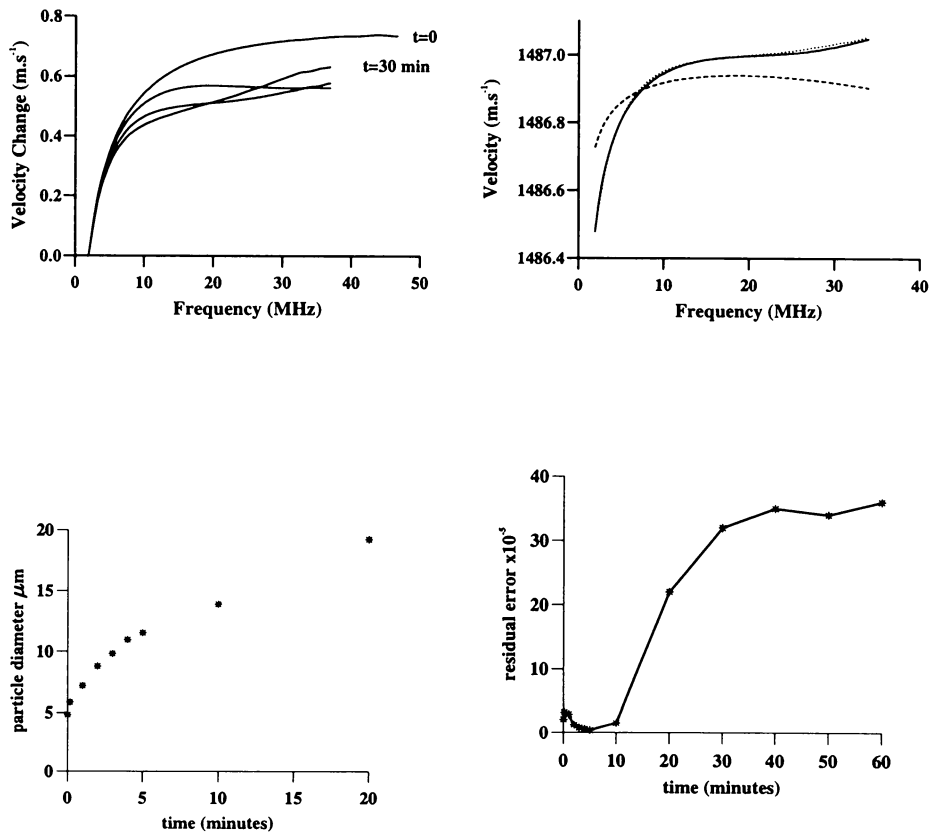

Figure 3. Ultrasonic wave propagation during flocculation of an aqueous emulsion of 1-bromohexadecane. Top left (a): Phase velocity change with respect to its value at 2MHz versus frequency at 0, 10, 20, 30 minutes of flocculation for the 0.026% HEC dose. Top right (b): Phase velocity spectra at 20 minutes: experimental data (dotted line); fitted Allegra & Hawley data, using a two bin size distribution (solid line); and a fit based on a single volume averaged particle size (broken line). Lower left (c): The larger of the two fitted particle sizes plotted versus time during flocculation. Bottom right (d): The 0.1% HEC dose flocculation: the mean squared error of the Allegra & Hawley fit to experimental phase velocity data plotted versus time into the flocculation.

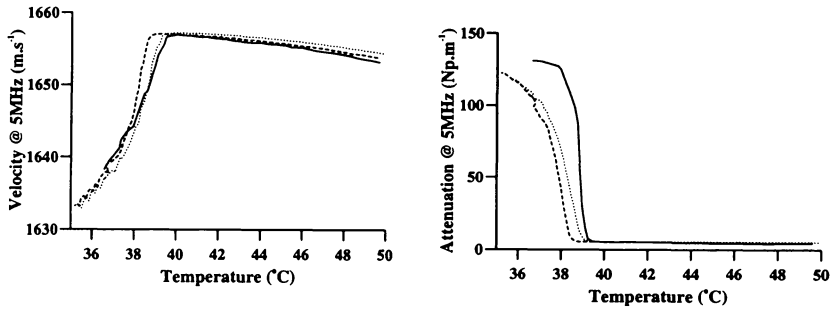

Figure 4. Ultrasonic wave phase velocity (left) and absorption coefficient (right) at 5 MHz during cooling crystallization of copper sulphate. Data from three consecutive experiments.

A Crystallization Experiment

We have adapted our ultrasonic spectrometer instrument to enable cooling crystallizations to be monitored. Solutions of copper (II) sulphate pentahydrate (23% - 25% w/w anhydrous) were cooled from 60°C to 30°C during which nucleation and subsequent crystal growth was observed 'by-eye' and ultrasonically. The crystallizations were not seeded and were not controlled by active manipulation of cell temperature, and so very rapid formation of crystals was expected. Figure 4 shows the ultrasonic phase velocity and the attenuation, both at 5 MHz, measured as the mixture crystallized. Three separate crystallizations from the same stock solution are included in the figure to demonstrate repeatability. Of interest is the temperature range over which crystallization occurred, nucleation taking place at 36.5°C, with crystallization complete at around 33°C. Comparison of our results with solubility curve data indicated a metastable zone width of around 6.5°. We are currently extending this work to use scattering theory in order to give a quasi-continuous measure of evolving crystal sizes during the reaction.

DISCUSSION AND CONCLUSION

In earlier work [11,12], we have demonstrated that scattering theory, and in some cases hydrodynamic theories, can give precise simulations of ultrasonic compression wave absorption coefficient $\alpha(\omega)$ and phase velocity $c(\omega)$ as functions of frequency. In this paper we have extended this work to examine the applicability of the Allegra and Hawley scattering model [6] to aqueous suspensions of small (30nm diameter) silica spheres; we have shown that the model as it stands produces an over estimate of absorption, and that if it is adapted so as to include an anomalous viscosity which is a rising function of frequency in the tens of MHz region, then good agreement is obtained with experimental data which we regard as reliable. Studies using hydrodynamic models [2,3], not included here, have also required adapted viscosity functions to obtain agreement between theory and experiment. Extensions to smaller particles (12nm diameter) yielded similar results. We are therefore of the opinion that the effects that we have observed are 'real', although we are conscious of the dangers in suggesting 'new' physical phenomena in the absence of formally derived theory, the development of which we hope to pursue at a later date.

In the case of the aqueous emulsion of l-bromohexadecane we have demonstrated that ultrasound can be used to track a flocculation reaction, and that adaptively fitting the Allegra and Hawley model to measured data gave excellent fits, and yielded a measure of

the evolving floc size. By calculating an error function representing the goodness of fit it was possible to detect when the flocculating emulsion began to form extended networks of particles rather than discrete flocs. We have also demonstrated that ultrasound can be used to track a crystallization reaction, and further work will involve modelling of the acoustic interactions with the changing mixture in order to obtain measures of the evolving crystal sizes. It is concluded that ultrasonic measurements combined with appropriate theory give a firm basis for the NDE of liquids containing particles, and for tracking and eventually controlling dynamic processes such as flocculation and crystallization.

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REFERENCES

1. A.H. Harker and J.A.G. Temple, J. Phys. D. 21, 1576-1588 (1988).
2. T.A. Strout, Phd Thesis, University of Maine, USA (1991).
3. A.S. Dukhin and P.J. Goetz, Langmuir 12, 4987-4997 (1996).
4. J.M. Evans and K. Attenborough, J. Acoust. Soc. Am. 102, 278-282 (1997).
5. P.S. Epstein and R.R. Carhart, J. Acoust. Soc. Am. 25, 553-565 (1953).
6. J. R. Allegra and S.A. Hawley, J. Acoust. Soc. Am. 51, 1545-1564 (1972).
7. L.L. Foldy, Phys. Rev. 67, 109-119 (1945).
8. P.C. Waterman and R. Truell, J. Math. Phys. 2, 512-537 (1961).
9. P. Lloyd and M.V. Berry, Proc. Phys. Soc. 91, 678-688 (1967).
10. R.E. Challis, J.A. Harrison, A.K. Holmes and R.P. Cocker, J. Acoust. Soc, Am. 90, 730-740 (1991).
11. A.K. Holmes, R.E. Challis and D.J. Wedlock, J. Coll. Int. Sci. 168, 339-348 (1994).
12. J.C. Austin, A.K. Holmes, J.S. Tebbutt and R.E. Challis, Ultrasonics, 34, 369-374 (1996).
13 D.A.R. Jones, B. Leary and D.V. Boger, J. Coll. Int. Sci. 147, 479-495 (1991).
14. D.W. Marquardt, J. Soc, Ind. Appl. Math. 11, 431- (1963).